

Plain Language Guide
to Understanding and Complying with the
Modified Test Methods Affecting
Centralized Waste Treaters.

February 19, 2003
US EPA Water Division
Water Enforcement Compliance Assurance Branch

EPA has modified pollutant test methods affecting Centralized Waste Treaters (CWTs) to cover additional pollutants and to change the quality control criteria. The modified methods (methods 625 and 1625) can be found in the current edition of Title 40 of the Code of Federal Regulations, Part 437. These additional pollutants were determined to be present in wastewater, after treatment, based on monitoring questionnaires sent to 20 selected CWT facilities. These pollutants were not tested for in previous versions of the test methods, therefore US EPA modified the two test methods to include them.

This guide should be helpful to:

- , Direct dischargers
- , Indirect dischargers
- , Local Regulators of Publicly Owned Treatment Works; and
- , State and Regional regulators

This guide covers:

- , What to look for in a laboratory
- , Understanding Modified Methods 625 and 1625
- , How to Evaluate Compliance data from Methods 625 and 1625

What to look for in a laboratory

A good lab will have readily available:

Quality Management Plan (QMP)

A QMP is the documentation of the lab's quality system. It serves as a blue print for the lab's management policies, objectives, organizational authority, roles and responsibilities ensuring that its data are the type and quality needed for their intended use.

Standard Operating Procedures (SOPs)

Routine technical (including lab analytical methods) and administrative activities are documented in SOPs. SOPs ensure consistency in the quality of products and processes.

Method Detection Limit Studies (MDLs)

On going Precision and Accuracy Data for analytical methods

Record of participation in Performance Evaluation Studies

Understanding Modified Method 625 for Organic
Chemical Analysis of Municipal and Industrial

Wastewater

Section 1 Scope and Application

This method covers organic compounds that are amenable to gas chromatography/mass spectroscopy and are listed in Tables 1 and 2. This method has stated limitations but may be extended to include other analytes. Method Detection Limits (MDLs) are provided, however specific waste waters may have different MDLs depending on the sample matrix. **This method is restricted in use to experienced analysts.**

Section 2 Summary of Method

A measured volume of sample is serially extracted with methylene chloride at basic and acidic conditions, dried, concentrated and analyzed by GC/MS. Identification of analytes is based on retention time and 3 characteristic masses (m/z). Concentration is determined using the internal standard technique with a single characteristic (m/z).

Section 3 Interferences

Basic extraction may reduce recovery of phenolic compounds. Packed columns limit analysis by incomplete resolution of certain isomeric compounds. Chemical ionization mass spectrometry is an option to address significant interferences.

Section 4 Safety

All Chemicals and compounds used in these procedures should be considered toxic and/or carcinogenic.

Section 5 Apparatus and Materials

Standard analytical instruments are used in this method. Temperature programmable Gas Chromatograph (GC) is required. The GC should utilize on column injection port, for packed columns or Split less injection, for capillary columns. The method identifies specific packed columns (3% SP-2250 and 1% SP-1240DA) for analyses, with the option to use other packed or capillary columns that meet stated requirements.

Section 6 Reagents

To avoid contamination analytical grade reagents are required for this method.

6.7 Stock standard solutions is modified to include additional analytes

Section 7 Calibration

- 7.2 Modify calibration standards to include analytes

Section 8 Quality Control

- 8.2 Modify precision and accuracy requirements to include additional analytes and associated performance criteria
- 8.3 Modify matrix spike to include additional analytes
- 8.4 Modify quality control check standard to include additional analytes

Section 9 Sample Collection, Preservation and Handling

Samples are collected as grab or composites. Samples must be in glass containers and refrigerated to prevent degradation. All samples should be extracted within seven days of collection and analyzed within 40 days.

Section 10 Separatory Funnel Extraction

Samples containers are marked for later measurement. Samples are spiked with appropriate surrogate solutions are serially extracted 3 times with aliquots 60 ml of methylene chloride adjusted to basic pH with sodium hydroxide. Sample are extracted again 3X 60 ml MeCl₂ adjusted to acidic pH. with sulfuric acid . Samples exhibiting excess emulsion are continuously extracted. Acid and basic Sample extracted are dried with sodium sulfate and concentrated on a hot water bath using Kuderna- Danish concentrators.

Section 11 Continuous Extraction

Samples are put into a distilling flask spiked with surrogate solutions, pH adjusted and charged with sufficient MeCl₂ and reagent water for 24 hour. Basic extracts are recovered. The pH of aqueous sample adjusted to acidic and re-extracted for an additional 24 hours. Basic and acidic extracts are dried, combined and concentrated as stated in Section 10.

Section 12 Daily GC/MS Performance Tests

GC/MS system performance is checked each day by evaluating DFTPP tuning criteria and benzidine's chromatographic tailing factors.

Section 13 Gas Chromatography/Mass Spectrometry

Tables 4 and 5 provide operating conditions, retention times and method detection limits that can be achieved using this method.

Section 14 Qualitative Identification

Pollutants are identified using retention time windows of +/- 30 seconds and Extracted Ion Current Profiles (EICPs) that are within +/- 20% of the peak height of authentic standards (obtained during the current run).

Section 15 Calculations

Pollutant concentrations are calculated based on response factor of the authentic standard, relative EICP response for the analyte and internal standard.

Section 16 Method Performance

Method Detection Limits (MDLs) listed in Tables 4 and 5 were obtained in reagent water. Actual MDLs will depend on instrument sensitivity and matrix effect. Additional method performance is attached below.

Section 17 Screening Procedure for 2,3,7,8-Tertachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

Understanding Modified Method 1625 Semi-Volatile
Organic Compounds by Isotope Dilution GC/MS

Note: All sections and figure numbers in this guide reference and correspond to section and figure numbers in EPA Methods 1625 an. The modified method found in 40 CFR Part 136 and 437 Effluent Limitations Guidelines, Pretreatment Standards, and New Source Performance Standards For the Centralized Waste Treatment Point Source Category; Final Rule 12/22/2000 Sections not listed here remain unchanged

Section 1 Scope and Application

This procedure is designed to meet the requirements of the CWA, RCRA and CERCLA programs. This analytical method is strictly for capillary column and is for use only by analysts experienced.

The applicable chemical compounds are listed in Tables 1-4 and for the CWT program expanded to include (1. 2. 3. 4.)

Typical Method Detection Limits are provided in Table 5 and 6

Section 2 Summary of Method

Samples are spiked with stable labeled analogs of the compounds of interest. Samples are extracted either continuously (waters < 1% solids) or ultra-sonically (solids >30%). Extracts are dried and concentrated and may be cleaned up using Gel Permeation Chromatography. Analytes are separated by GC and detected using Mass Spectroscopy. The Spiked analogs correct for analytical variability.

Pollutants in samples are identified using:

1. Authentic standards agreeing in retention time and mass spectra
2. Reference Standards (listed in method) agreeing in retention time and mass spectra
3. Tentative comparison with EPA/NIH Spectra File

Pollutant concentrations are determined by Extracted Ion Current Profiles (EICP) using:

1. Authentic standards and labeled analogs (isotope dilution technique)
2. Authentic standards with out labeled analog s(internal standard technique)
3. With out standards (known response factors)
4. Unknown response factors (ratios of EICP areas for analytes and internal standards)

Section 3 Contamination and Interferences

Contamination may be introduced through sample processing hardware. 1 method blank for each sample on an 8 hour shift is used to demonstrate the system is contamination free.

Section 4 Safety

All Chemicals and compounds used in these procedures should be considered toxic and/or carcinogenic.

Section 5 Apparatus and Materials

Standard analytical instruments are used for this method.

Section 6 Reagents and Standards

- 6.7 Modify stock standard solutions to include additional analytes
- 6.8 Modify labeled compound solution to include additional labeled compounds
- 6.9 Modify secondary standard to include additional analytes in tables 1&2.
- 6.12 Solutions for obtaining authentic mass spectra must include additional analytes
- 6.13 Modify calibration standards to include additional analytes in tables 1, 2 and labeled compounds in tables 5 and 6.
- 6.14 Modify precision and recovery standard to include additional analytes
- 6.15 Solutions containing additional analytes are to be analyzed for stability

Section 7 Calibration

- 7.2.1 Modified to include analytes listed in tables 1 and 2 and the labeled compounds in tables 5 and 6
- 7.4.5 Modify to include analytes in table 1 and 2 and labeled compounds in tables 5 and 6 in the calibration.

Section 8 Quality Assurance/Quality Control

- 8.2 Modify initial Precision and Recovery (IPR) requirements to include tables 1 and 2 and labeled compounds in tables 5 and 6. Additional criteria provided in table 7.
- 8.3 Include Table 3 &4 labeled compounds in performance tests. Additional criteria in table 7.
- 8.5.2 Include analytes in Table 1 &2 in blank acceptance criteria.

Section 9 Sample Collection, Preservation and Handling

Samples are collected as grab or composites..Samples must be in glass containers and refrigerated to prevent degradation. All samples should be extracted within seven days of collection and analyzed within 40 days.

Section 10 Sample Extraction, Concentration and Cleanup

Samples are spiked with stable labeled analogs of the compounds of interest. Samples are extracted either continuously (waters < 1% solids) or ultra-sonically (solids >30%). Extracts are dried and concentrated and may be cleaned up using Gel Permeation Chromatography. Analytes are separated by GC and detected using Mass Spectroscopy. The Spiked analogs correct for analytical variability.

10.12 Include Tables 5 & 6 labeled compounds.

10.13 Include Tables 5 & 6 labeled compounds precision and recovery criteria.

Section 11 GC/MS Analysis

Section 12 System and Laboratory Performance

12.5 Include Table 7 additional quality control requirements for calibration verification.

12.7 Include Table 7 additional quality control requirements for ongoing precision and recovery.

Section 13 Qualitative Determination

Pollutants are identified through use of mass spectral libraries. Some pollutants are identified as using known retention time windows and Extracted Ion Current Profiles (EICPs). Other pollutants are tentatively identified using an NIH/EPA library.

Section 14 Quantitative Determination

Pollutant concentrations are either calculated using the internal standard method or the isotope dilution method.

Section 15 Analysis of Complex Samples

This method is capable of dealing with a variety of analytical challenges through use of alternative quantitation schemes.

Section 16 Method Performance

Inter-laboratory validation results were published by US EPA in June 1984.

How to Evaluate Modified 625 and 1625 Data

Laboratories reporting data to the CWT should identify:

1. Evidence of chain of custody

- Name of lab
- Name of sampler
- Name of analyst
- Sample identification

2. Sample Stream

- Sample matrix (identify waste stream type: oily, metal, organic or mixed or use subparts)
- Sampling location
- Sampling method - Grab vs. 24 hr. composite

3. Holding Times

- Date/time of sampling
- Date/time of sample preparation
- Date/time of analysis
- Sample preservation - include temperature

4. Compliance Data

- complete list of parameters analyzed should correspond to attached list for each specified waste stream
- Analytical method used: modified 625/1625
- Method Detection Limit
- Measured concentration compared to control

document

The first four should be done for each compliance determination. If questions still arise ask the CWT for the items in number 5.

5. **Quality Control**

- Method blank- lab contamination
- Method Detection Limit
- Matrix spikes- interferences
- Field blanks- sampling contamination
- Lab/field duplicates- analytical and process reproducibility
- Analytical run sequence- adherence to method specifications
- Surrogates- extraction efficiency
- Internal standards- instrumental reproducibility